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(54) **MOLDED POLYURETHANE FOAM WITH ENHANCED PHYSICAL PROPERTIES**

POLYURETHAN FORMSCHAUM MIT VERBESSERTEN PHYSIKALISCHEN EIGENSCHAFTEN

MOUSSE DE POLYURETHANE MOULEE PRESENTANT DES PROPRIETES PHYSIQUES  
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**EP 0 865 457 B1**

**Description****Technical Field**

5 [0001] The present invention pertains to molded, flexible polyurethane foam prepared by the prepolymer process. More particularly, the present invention pertains to molded polyurethane flexible foams prepared from isocyanate-terminated prepolymers derived from the reaction of an excess of di- or polyisocyanate with a polyol or polyol component prepared by double metal cyanide complex catalysis having an unsaturation of less than 0.03 milliequivalents of unsaturation/per gram of polyol (meq/g). The molded foams display enhanced physical properties in addition to displaying  
 10 excellent processing latitude. The foams are preferably all-water blown.

**Background Art**

15 [0002] High resiliency (HR) polyurethane slab foam is now a high volume commercial product. HR slab foam is generally all-water blown and may be made by either prepolymer or one-shot technology. However, slab foam, while eminently suitable for applications such as carpet underlay and flat cushioning material for furniture, is unsuitable for applications which require contoured parts, for example automotive seating. For such applications, molded polyurethane foam is generally used. In molded foam, the foam forming ingredients are mixed and injected into a closed mold, which may be heated to 150-300°C (hot molding) or 30-70°C (cold molding). The admixture of multiple streams  
 20 into the mix head is termed a "one-shot" process.

[0003] Because molded foam cannot rise unrestrained, as is the case with slab foam, the respective formulations are quite different. Even with different formulations, processing of molded foam is considerably more difficult than processing of slab foam, and often gives rise to a high scrap rate. A further difference between molded foam and slab foam is that the former must be crushed mechanically prior to complete cure, either by hand or by the use of rollers or  
 25 similar devices. Alternatively, the foam may be "crushed" *in situ* through the use of timed pressure release (TPR) as disclosed in U.S. Patent No. 4,579,700; by timed partial pressure release (TPPR); or by a combination of TPR and reduced mechanical crushing as disclosed in U.S. Patent No. 4,717,518. The foregoing TPR patents are licensed worldwide.

[0004] Prepolymer technology has certain advantages over one-shot technology. Foams produced by prepolymer technology are subject to less processing related variation due to the use of fewer reactive chemical streams as opposed to one-shot foams. The polymer structure is also more controllable in prepolymer foams. Moreover, the use of prepolymer techniques allows the foam manufacturer to inventory fewer components. Although much early work in polyurethane foam technology centered on prepolymer techniques, today most flexible foam is produced by one-shot technology. With respect to molded foams, virtually all systems are one-shot. The reasons why prepolymer technology  
 35 is not in widespread use in molded foam have to do with the nature of the molding process as opposed to the slab process.

[0005] For example, in the well known treatise on polyurethanes: "POLYURETHANES: CHEMISTRY AND TECHNOLOGY", J.H. Sanders and K.C. Frisch, Interscience Publishers, N.Y., p.99, the authors indicate that even one-shot technology was difficult with molded foam, and that completely satisfactory prepolymer systems were never fully  
 40 achieved. Not only is the scrap rate cited as being high, particularly with regard to surface defects, but cure cycles are inordinately long in molded foams prepared from prepolymers. One-shot technology has reduced material usage due to decreased scrap rates, reduced labor costs, and eliminated lengthy curing cycles.

[0006] R.E. Knox, in "Molding of Prepolymer Based Resilient Urethane Foam", RUBBER WORLD, February 1959, pp. 685-692, has documented some of the defects, particularly surface defects, associated with prepolymer molded  
 45 foam. Cited as assisting elimination of surface defects is the use of brushing or spray-coating the mold surface with surface active agents. However, this process involves additional steps which increase manufacturing costs.

[0007] Attempts to overcome the problems associated with molded polyurethane foams via prepolymers have generally focused on adjusting such variables as type of catalyst, catalyst levels, catalyst combinations, type and amount of cross-linker, isomer content of the isocyanate component, polyether polyol blends, and the like. However, while  
 50 isolated, successful systems have been sometimes prepared, these systems still suffer in terms of processing latitude as well as lacking the flexibility to readily accommodate desired changes in such physical properties such as density, foam softness, and the like. Fundamental changes in the nature of the prepolymer ingredients have not been proposed.

[0008] An example of the types of formulation adjustments referred to above is disclosed in U.S. Patent No. 5,070,114, wherein water-blown, molded polyurethane foams are prepared from isocyanate-terminated prepolymers derived from methylenediphenylenediisocyanate (MDI) blends containing minimally 2 weight percent of 2,4'-MDI isomers. However, no molded foams are exemplified, only free rise foams having been produced.  
 55

[0009] In "Production of Soft Block Foams and TDI-Based Cold Cure-Molded Foams With No Use of CFCs", 32ND ANNULAR POLYURETHANE TECHNICAL MARKETING CONFERENCE, October 1-4, 1989, G.F. Lunardon et al.,

hypersoft molded foams are prepared from toluene diisocyanate-based prepolymers and a special polyether polyol having a high ethylene oxide content, supplied as a separate stream. Polyether polyols with high terminal oxyethylene content are commonly utilized in one-shot molded foams due to the higher reactivity associated with high primary hydroxyl content, generally above 70 mol percent. However, appreciable amounts of such high ethylene oxide content polyols may undesirably affect numerous physical properties in humid environments. The resulting foams had relatively low resiliency and high compression set.

[0010] Polyoxyalkylene polyether polyols utilized in polyurethane foam production are conventionally manufactured by the base-catalyzed oxyalkylation of a two to eight-functional initiator molecule, generally using propylene oxide or mixtures of propylene oxide and ethylene oxide as the alkylene oxide. For one-shot molded polyurethane foams where high primary hydroxyl content is required, i.e., higher than 70 mol percent, the polyols are capped with polyoxyethylene moieties by employing solely ethylene oxide during the last stages of oxyalkylation. Use of such polyols often leads to problems in humid environments where absorption of water plasticizes the polyurethane.

[0011] During preparation of polyoxypropylene polyether polyols by base catalysis, a competing rearrangement of propylene oxide to allyl alcohol introduces unsaturated monols into the reaction mixture which themselves serve as mono-functional initiator molecules. The result is a gradual dilution of functionality and continued production of polyoxyalkylene monol of lower molecular weight. As a result, base-catalyzed polyol equivalent weight is limited to about 2000 Daltons (Da). Even at this modest equivalent weight, the functionality of a polyoxypropylene diol may be reduced from its nominal, or theoretical, functionality of 2 to the range of 1.5 - 1.7 or less. The product may contain as much as 40-45 or more mol percent monol, the monol fraction having a broad molecular weight distribution as well.

[0012] In the decade of the 60's, double metal cyanide complex catalysts (DMC catalysts) were developed for alkylene oxide polymerization. However, due to their greatly increased cost as compared to simple basic catalysts, and limited polymerization rate, such catalysts had not been widely used, despite their ability to produce polyoxyalkylene polyols with low unsaturation and low monol content. Non-stoichiometric metal cyanide complex catalysts, as disclosed, for example, in U.S. Patent Nos. 5,100,997, 4,477,589, 5,158,922, and 5,248,833 have exhibited increased polymerization rates as compared to the first generation DMC catalysts and have lowered unsaturation to the range of 0.015 - 0.018 meq/g in polyols in the c.a. 2000 Da equivalent weight range. However, the amount of catalyst required is still relatively high in view of catalyst cost. Most recently, however, the assignee of the present invention has developed highly efficient double metal cyanide complex catalysts which not only may be used in much smaller amounts than previously possible, but moreover provide polyoxyalkylene polyols with exceptionally low unsaturation, i.e., in the range of 0.002 to 0.007 meq/g. The measured functionality of such polyols closely approaches the nominal initiator functionality. Moreover, the polyols display a very narrow molecular weight distribution, as reflected by polydispersities ( $M_w/M_n$ ) generally less than c.a. 1.2. Suitable methods of preparation are disclosed in EP-A-0654302 and EP-A-0700949. The

[0013] Double metal cyanide catalysis has certain drawbacks with respect to polyoxyethylene capped polyols, however. It has been discovered that terminating DMC-catalyzed alkylene oxide polymerization with ethylene oxide, rather than resulting in high primary hydroxyl, oxyethylene capped polyols, results in complex products believed to contain considerable quantities of homopolyoxyethylene. Thus, preparation of ethylene oxide capped polyethers employing double metal cyanide catalysts has required denaturing the double metal cyanide catalyst with base such as potassium hydroxide and continuing addition of ethylene oxide in a traditional base-catalyzed oxyalkylation. This adds significant cost and complexity to the polyol preparation process.

[0014] Although numerous benefits have been ascribed to the use of DMC-catalyzed polyoxyalkylene polyols, such polyols are not drop-in replacements for conventionally catalyzed polyols, for reasons not completely understood, but at least in major part due to the differences in monol content, actual functionality, and molecular weight distribution which lead to different polymer microstructure.

[0015] For example, as shown by R.E. Bolin et al., "Properties of Urethane Foams Related to Molecular Structure", J. CHEM. AND ENG. DATA, v.4, No. 3, July 1959, pp. 261-265, use of higher molecular-weight polyols increases the molecular weight between branch points in the cross-linked polyurethane structure, and as a result, increases tensile elongation while decreasing tensile strength. At the same time, compression strength decreases as well, resulting in softer, more extensible foams. Thus, use of higher equivalent weight polyols, made possible through DMC-catalyzed oxyalkylation, should result in a softer, more extensible foam. However, R.L. Mascioli, "Urethane Applications for Novel High Molecular Weight Polyols", 32ND ANNUAL POLYURETHANE TECHNICAL/MARKETING CONFERENCE, Oct. 1-4, 1989, pp. 139-142, indicates that substitution of a double metal cyanide complex-catalyzed, low unsaturation 10,000 Da triol in a typical flexible foam formulation, rather than produce a softer, more extensible foam, produced a stiff and boardy product. J.W. Reisch et al. in "Polyurethane Sealants and Cast Elastomers With Superior Physical Properties", 33RD ANNUAL POLYURETHANE TECHNICAL MARKETING CONFERENCE, Sept. 30 - Oct. 3, 1990, on page 368, indicates that substitution of a low unsaturation polyether polyol for a conventional, base-catalyzed polyol of higher unsaturation led to increased hardness in elastomers prepared from such polyols. While not directed to the present field of endeavor, the increased hardness of the elastomers mitigates against use of such polyols in poly-

urethane foams, where decreased hardness is generally the goal. Moreover, as the inventors of the present invention disclose below, in a one-shot molded polyurethane foam formulation, substitution for a conventionally catalyzed triol having a measured functionality of 2.2 by a DMC-catalyzed diol/triol blend having similar (2.3) functionality led to total foam collapse.

[0016] It would be desirable to provide to the polyurethane foam industry, a prepolymer composition suitable for preparing molded polyurethane foams with acceptable processing time and latitude. It would be further desirable to provide foam formulations which result in enhanced physical properties of the molded foam product. It would be yet further desirable to offer prepolymer foam formulations which allow for taking advantages of the unique properties of double metal cyanide catalyzed polyoxyalkylene polyols, without requiring high primary hydroxyl content.

### **Summary Of The Invention**

[0017] It has now been surprisingly discovered that prepolymer-based molded polyurethane foams may be prepared from isocyanate-terminated prepolymers based on low-unsaturation polyoxyalkylene polyols prepared by double metal cyanide complex catalysis. Moreover, it has been further surprisingly discovered, that not only do these prepolymers offer wide processing latitude and short cure cycles, but moreover, the molded polyurethane foams thusly prepared exhibit superior physical properties in virtually all categories, including vastly improved 50% wet compression set (wet set). Seldom is it possible to increase nearly all foam physical properties without a trade-off in terms of other properties.

### **Description of the Preferred Embodiments**

[0018] The prepolymer foams of the subject invention are prepared by introducing the prepolymer formulations of the subject invention together with water and optionally auxiliary blowing agents and additives into a closed mold, allowing the reactive ingredients to foam, and recovering a molded, foamed polyurethane product. The isocyanate index of the reactive ingredients is advantageously between 70 and 130, preferably between 90 and 110, and most preferably c.a. 100. By the term "closed mold" is meant a mold which prevents unrestrained rise of foam. Such molds may be clamped in a closed condition following which the polyurethane reactive ingredients are injected into the mold cavity, or may be open molds into which the reactive ingredients are poured or metered, the mold being subsequently closed. Most such molds contain one or more vents which may be monitored to ascertain progress of the reaction. Such molds are closed molds as viewed by one skilled in the art.

[0019] The prepolymers of the subject invention are prepared by conventional prepolymer techniques employing an excess of di- or polyisocyanate or mixture thereof, but employing as the polyol component, a polyol component prepared by double metal cyanide complex catalysis having a measured unsaturation of less than 0.03 meq/g, preferably less than 0.02 meq/g, and most preferably, less than 0.01 meq/g as measured by ASTM D-2849-69, "Testing of Urethane Foam Polyol Raw Materials". The polyol component used to prepare the prepolymers may comprise polyoxyalkylene polyether polyols in their entirety, mixtures of polyoxyalkylene polyether polyols with polymer-modified polyoxyalkylene polyether polyols as hereinafter described, or minor quantities of other, hydroxyl-functional polyols such as polyester diols, amino-terminated polyoxyalkylene polyether polyols, and other isocyanate-reactive polyols.

[0020] By polyoxyalkylene polyether polyol is meant a polyol derived from the additional polymerization of a vicinal alkylene oxide. Polyols prepared entirely from non-vicinal cyclic oxides such as oxetane and tetrahydrofuran are not polyoxyalkylene polyether polyols as that term is defined herein, although such polyols may be included in the polyol component. The "measured unsaturation" of the polyol component is the measured value, or weight average of measured values of the polyoxyalkylene polyether polyol portion of the polyol component only.

[0021] The polyoxyalkylene polyether polyols of the prepolymer polyol component are prepared by the double metal cyanide complex-catalyzed oxyalkylation of a suitable initiator molecule or mixture thereof. Non-limiting examples of suitable initiator molecules are di- to octa-functional initiators such as water, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, hydroquinone, bisphenol A, neopentylglycol, cyclohexanediol, cyclohexanedimethanol, 2,2,4-trimethyl-1,5-pentanediol, glycerine, trimethylolpropane, pentaerythritol, dipentaerythritol,  $\alpha$ -methylglucoside, sorbitol, mannitol, sucrose, methylol group-containing phenol/formaldehyde condensates, and the like.

[0022] Preferred nominal initiator functionality is from 2-6, preferably 2-4, and most preferably 2-3.

[0023] Particularly when metal naphthenates or other low-unsaturation producing catalysts are used, amino-group containing initiators such as the various toluene diamine isomers, ethylene diamine, propylene diamine, tetrakis [2-hydroxyethyl- and 2-hydroxypropyl]ethylene diamine, alkanol amines such as triethanol amine, diethanol amine, and monoethanol amine, aniline, methylenedianiline, diethylene triamine, and the like may be used as well. Thus, while it is preferred to employ DMC-catalysis to produce the polyoxyalkylene polyether polyols, other catalysts capable of producing low-unsaturation polyols may be used as well. Blends of initiator molecules may also be used, as well as blends of polyoxyalkylene polyether polyols individually prepared from single or multiple initiators. The preferred overall functionality of the polyol component used to form the isocyanate-terminated prepolymers of the subject invention

ranges from about 2.3 to about 4, more preferably about 2.5 to 3.5.

[0024] Because low molecular weight initiators, particularly those with vicinal hydroxyl groups, may cause undesirably long induction periods and/or lower rates of oxyalkylation when oxyalkylation is catalyzed by DMC catalysts, polyoxyalkylene oligomers prepared from the foregoing or other initiators may advantageously be employed rather than the monomeric, low molecular weight initiators themselves. Thus, oligomeric polyoxyalkylene polyol initiators having equivalent weights of from 100 to 1000 Da, preferably 100-600 Da are preferred. Such oligomeric polyoxyalkylene polyol initiators may be prepared by conventional base catalyzed oxyalkylation of the respective monomeric, low molecular weight initiator, following which the basic catalyst residues are removed or inactivated by neutralization, treatment with an adsorbent such as magnesium silicate followed by filtration, removal using ion exchange, etc. Other methods of preparing the oligomeric polyoxyalkylene polyol initiators are suitable as well.

[0025] The oxyalkylation of the initiator molecules is conducted with one or more higher alkylene oxides, optionally in admixture with ethylene oxide. By "higher alkylene oxide" is meant an alkylene oxide having 3 or more carbon atoms, for example, propylene oxide, 1,2- and 2,3-butylene oxide, C<sub>5</sub>-C<sub>18</sub>  $\alpha$ -olefin oxides, epichlorohydrin, and the like. Preferred are propylene oxide and butylene oxide, the former being most preferred. Use of mixtures of ethylene oxide and one or more higher alkylene oxides leads to essentially random copolymers. The ratio of higher alkylene oxide to ethylene oxide may be changed during oxyalkylation to produce multiple block polyols containing blocks of all higher alkylene oxide-derived moieties and/or one or more blocks of higher alkylene oxide/ethylene oxide moieties. Polymerization solely with ethylene oxide should be avoided when employing DMC catalysis.

[0026] The polyoxyalkylene polyols preferably contain from 0 to 25 weight percent more preferably 5 to 25 weight percent, and most preferably 5 to 20 weight percent oxyethylene moieties, present randomly or as a cap. Random oxyethylene moieties, as explained previously, may be incorporated simply by adding ethylene oxide along with higher alkylene oxide during oxyalkylation in the presence of a DMC-catalyst or other low-unsaturation producing catalyst. To prepare polyoxyethylene capped polyols, it is necessary to conduct oxyethylation with other than DMC catalysts, preferably, but not limited to, basic catalysts such as sodium or potassium hydroxides or alkoxides.

[0027] When oxyethylene-capped polyoxyalkylene polyols are desired, and the propylene oxide or mixed propylene oxide/ethylene oxide polymerization has been effected with DMC-catalysts, the DMC catalysts or catalyst residues may be removed prior to introduction of conventional oxyalkylation catalysts if desired, but preferably, a basic catalyst is simply added without resort to DMC catalyst removal. The basic catalyst deactivates the DMC catalyst, permitting capping with oxyethylene moieties to prepare polyoxyalkylene polyether polyols having primary hydroxyl content ranging up to 100 mol percent. Preferably, however, the primary hydroxyl content is from 0 mol percent to about 70 mol percent, more preferably 0 mol percent to 50 mol percent, and most preferably 0 to 30 mol percent. It is most surprising that polyoxyalkylene polyether polyols prepared by DMC-catalyzed polymerization of mixtures of higher alkylene oxide and ethylene oxide, having no "cap" and having primary hydroxyl content less than 50 mol percent, advantageously less than 30 mol percent, are suitable for preparation of molded polyurethane foam, allowing polyol preparation without a separate oxyethylene capping step.

[0028] Regardless of their manner of preparation, the polyoxyalkylene polyether polyols, whether capped or not, have a weight average measured unsaturation of less than 0.03 meq/g polyol as measured by ASTM D-2849-69, preferably less than 0.02 meq/g, more preferably less than 0.01 meq/g. If the weight average unsaturation of the polyoxyalkylene polyether polyol portion of the polyol component, as herein defined, is not less than 0.03 meq/g, foams having the desired properties will not be obtained.

[0029] Polymer-modified polyols, when employed in the polyol component, are preferably prepared from the low-unsaturation polyoxyalkylene polyols previously described. Preferred polymer-modified polyols are prepared by the *in situ* polymerization of one or more vinyl monomers in the polyoxyalkylene polyol, variously termed the "base" or "carrier" polyol. Preferred vinyl monomers are acrylonitrile and styrene, although other monomers such as the various acrylates, methacrylates, and other vinyl monomers may be used as well. Methods for the *in situ* polymerization are well known to those skilled in the art, for example as evidenced by U.S. Patent Nos. 3,383,351, 3,953,393, and 4,119,586. The polyoxyalkylene polyether base or carrier polyol is included when measuring or calculating the average unsaturation of the polyoxyalkylene polyether polyol portion of the polyol component.

[0030] In addition to the aforementioned polyvinyl polymer-containing polymer-modified polyols, polymer polyols may also be prepared by the addition of finely ground polymer particles or the *in situ* size-reduction of larger particles to form stable dispersions. Dispersions prepared by the reaction of isocyanates with various amino-functional, hydroxyl-functional, or combined amino/hydroxyl functional monomers to form the so-called PUD (polyurea dispersion) polyols, PID (polyisocyanurate dispersion) polyols, PIPA (reaction product of isocyanates with alkanolamines), PHD polyols, and the like, may also be used. All these polyols are well described in the literature. PHD and PIPA polyols are recognized commercial products.

[0031] The polyol component should have an average equivalent weight of from 1000 Da to 5000 Da, preferably 1500 Da to 5000 Da, and most preferably about 1500 Da to 3000 Da. Equivalent weights and molecular weights expressed herein in Daltons (Da) refer to number average weights unless otherwise specified. The average hydroxyl

number of the polyol component may range from 10 to 80, more preferably 10 to 56, and most preferably 15 to 35.

[0032] The polyol component may comprise but a single polyoxyalkylene polyol, a blend of polyoxyalkylene polyols, a single polyoxyalkylene polymer-modified polyol, or a blend of polyoxyalkylene polyols and polymer-modified polyoxyalkylene polyols. The polyol component may further comprise hydroxyl functional polyesters, amino-functional polyoxyalkylene polyols and the like. The polyoxyalkylene polyols of the polyol component, whether conventional (non-polymer-modified) or polymer-modified polyols, are all preferably prepared with catalysts such that unsaturation is minimized. However, polyoxyalkylene polyols or polymer-modified polyoxyalkylene polyols prepared by base catalysis or other methods of catalysis which result in higher levels of unsaturation than 0.03 meq/g may be used, provided that the total unsaturation of the polyoxyalkylene polyether polyol portion of the polyol component is less than the previously defined limits, i.e., less than 0.03 meq/g, most preferably less than 0.01 meq/g.

[0033] The isocyanate components useful in preparing the isocyanate-terminated prepolymers of the subject invention include the known aromatic and aliphatic di- and polyisocyanates, for example 2,4- and 2,6-toluene-diisocyanates and mixtures thereof (TDIs), 2,2'-, 2,4'- and 4,4'-methylene diphenylene diisocyanates and mixtures thereof (MDIs), polymethylene polyphenylene polyisocyanates (PMDIs), 1,6-hexanediisocyanate, isophoronediiisocyanate, and mixtures of such isocyanates. Other isocyanates may be used as well. Also suitable are the so-called modified isocyanates prepared by reacting a di- or polyisocyanate with an isocyanate-reactive monomer or oligomer or with themselves. Examples are urethane-modified isocyanates prepared by reacting a di- or polyisocyanate or mixture thereof with one or more glycols, triols, oligomeric polyoxyalkylene diols or polyols or mixtures thereof; urea modified isocyanates prepared by reacting the isocyanate with a diamine or amino-terminated polyoxyalkylation polyether oligomer; and carbodiimide, polyisocyanurate, uretonimine, allophanate and uretidione modified polyisocyanates prepared by reacting the isocyanate or modified isocyanate with itself in the presence of a suitable catalyst. Such isocyanates and modified isocyanates are well established items of commerce. Particularly, preferred di- and/or polyisocyanates include TDIs, MDIs, PMDIs and mixtures of these, particularly mixtures of TDIs and MDIs, the latter preferably containing a substantial majority of the 4,4'-isomer.

[0034] The prepolymers of the subject invention are prepared in the conventional manner by reacting the polyol component with the isocyanate component with or without urethane promoting catalysts, as described, for example, in the POLYURETHANE HANDBOOK, Gunter Oertel, Hanser Publishers, Munich © 1985, POLYURETHANES: CHEMISTRY AND TECHNOLOGY, J.H. Saunders and K.C. Frisch, INTERSCIENCE PUBLISHERS, New York, 1963, and in U.S. Patent No. 5,070,114, herein incorporated by reference. Continuous and batch processes for the preparation of isocyanate-terminated prepolymers are disclosed in "Continuous Processing of Urethane Foam Prepolymers", J.R. Wall, CHEMICAL ENGR. PROGRESS, V. 57, No. 10, pp. 48-51; Sanders, *op.cit.*, Part II, pp. 38-43; U.S. Patent No. 5,278,274; European published application EP 0 480 588 A2; and Canadian Patent No. 2,088,521.

[0035] The prepolymers of the subject invention have a free isocyanate (NCO) group content of from 5 weight percent to 35 weight percent, preferably 6 weight percent to 25 weight percent, and advantageously 8 to 20 weight percent.

[0036] The isocyanate-terminated prepolymers comprise the A-side (iso side) of the molded polyurethane foam system. The B-side (resin side) of the subject invention molded polyurethane foam system employs isocyanate reactive components, blowing agent(s), surfactant(s), and other additives and auxiliaries, for example chain extenders, cross-linkers, catalysts, dyes, pigments, fillers, etc. One or more of the B-side components may, in the alternative, be included with the A-side components.

[0037] Catalysts are generally necessary. The catalysts may be selected from conventional urethane-promoting catalysts, for example, tin catalysts such as dibutyltin diacetate, dibutyltin dilaurate, stannous octoate, and the like; amine catalysts such as NIAx®A-1, diethylene triamine, 1,4-diazabicyclo[2.2.2]octane, and the like. Mixtures of metal catalysts and amine catalysts may be used as well. Preferred are amine catalysts. Amounts of catalysts may be readily determined by one skilled in the art, and may range, for example, from 0.1 to 5 weight percent based on the weight of the foam.

[0038] Suitable chain extenders include the various alkylene glycols and oligomeric polyoxyalkylene glycols with molecular weights up to about 300 Da, for example ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, tripropylene glycol, and the like. The amount of chain extender may be adjusted to provide the necessary processing or physical parameters of the foam. Preferably, only most minor amounts of chain extenders are used, for example less than 10% by weight and preferably less than 5% by weight relative to foam weight. Aminofunctional chain extenders such as MOCA, toluene diamine, and hindered aromatic amines may also be suitable.

[0039] Suitable cross-linkers include polyhydroxyl functional monomeric compounds such as glycerine, but preferably alkanolamines such as monoethanolamine, diethanolamine (DEOA) and triethanolamine (TEOA). As with the chain-extendors, cross-linkers, when used, are preferably used in most minor amounts, for example less than 10 weight percent and most preferably less than 5 weight percent relative to total foam weight. Both chain extenders and cross-linkers, when used, are preferably dissolved in water which serves as the blowing agent.

[0040] A cell-stabilizing surfactant is generally required. Suitable cell-stabilizing surfactants include the various or-



ganopolysiloxanes and polyoxyalkylene organopolysiloxanes as are well known to those skilled in the art. Suitable surfactants include DC5043 available from Air Products, and Y-10,515 available from OSI, Inc. Additional surfactants are available from Wacker Silicones, Adrian, MI, and Goldschmidt A.G., Germany. Combinations of surfactants may also be used, for example, a blend of Tergitol 15-S-9 available from the Union Carbide Corporation and DC5043. The amount of surfactant should be an amount effective to avoid foam collapse, and is readily ascertained by one skilled in the art. Amounts of from 0.1 to about 5 weight percent, preferably 0.5 to 2 weight percent based on the weight of the foam may be suitable.

[0041] The B-side may further contain polyoxyalkylene polyols and/or polymer-modified polyoxyalkylene polyols wherein the polyols have molecular weights of c.a. 300 Da or higher, preferably equivalent weights of from 500 to 5000, more preferably 1000 to 3000. Up to about 50 weight percent of total polyol, preferably up to 25% of total polyol may be contained in the B-side as opposed to the prepolymer, as the polyol contained in the prepolymer does not have to react, being already incorporated into the prepolymer. Most preferably, the prepolymer contains in excess of 90% of total polyol, and in particular virtually all polyol. For the same reason, high primary hydroxyl content is not necessary for any B-side polyol. However, B-side polyols may advantageously contain greater than 50 mol percent, and more preferably greater than 70 mol percent primary hydroxyl groups. Preferably, no additional polyoxyalkylene polyol is contained in the B-side formulation.

[0042] The B-side contains one or more blowing agents of the chemical and/or physical type. The preferred blowing agent is water, which reacts with isocyanate to generate urea linkages with concomitant release of carbon dioxide gas. Physical blowing agents may also be used, either alone or in conjunction with water. Non-limiting examples of additional blowing agents include the lower alkanes, e.g., butane, isobutane, pentane, cyclopentane, hexane, and the like; the chlorofluorocarbons (CFCs), e.g. chlorotrifluoromethane, dichlorodifluoromethane, and the like; the hydrochlorofluorocarbons (HCFCs) such as fluorodichloromethane and chlorodifluoromethane; the perfluorinated C<sub>3</sub>-C<sub>8</sub> aliphatic and cycloaliphatic hydrocarbons (PFCs) and substantially fluorinated analogous (HPFCs); chlorinated hydrocarbons such as methylenedichloride, liquid CO<sub>2</sub>, and the like. CFC's are preferably avoided due to environmental concerns. As stated previously, the preferred blowing agent is water, which is most preferably used as the sole blowing agent. Frothing agents such as CO<sub>2</sub>, nitrogen, and air may be introduced as well.

[0043] The amount of blowing agent is selected so as to provide a foam density of from about 1.0 lb/ft<sup>3</sup> or less to 4.0 lb/ft<sup>3</sup> or more, more preferably 1.0 lb/ft<sup>3</sup> to 3.0 lb/ft<sup>3</sup>, and most preferably about 1.2 lb/ft<sup>3</sup> to about 2.8 lb/ft<sup>3</sup>. Amounts of water ranging from 1.0 part to 7.0 parts per 100 parts of total polyol component, preferably 2.0 parts to about 6.0 parts are especially preferred.

[0044] The A-side and B-side are combined in conventional fashion employing a low pressure or high pressure mix head and introduced into the mold which is optionally and preferably maintained above ambient temperature. The mold temperature may be maintained at a temperature suitable for either hot or cold molding. The mold may be closed, with foam forming ingredients introduced into a suitable charging port, or may be an open mold which is closed following introduction of the foam formulation. The foam is cured, demolded, TPRed and/or crushed, and cured in the conventional manner. It has been surprisingly discovered that not only do the foam formulations of the subject invention process well, but moreover, the foams are of superior quality as compared to conventional foams from similar systems. Moreover, these results are achievable from polyols independent of primary hydroxyl content normally required to produce molded foam.

[0045] Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

#### Comparative Examples 1 and 2

[0046] Two "one-shot" formulations as set forth in Table 1, one containing a low monol polyol in the B-side, the second containing a conventional EO-capped, KOH-catalyzed polyol with much higher unsaturation but similar polyol functionality. As can be seen, low unsaturation polyols of low primary hydroxyl content do not produce foam in typical HR fashion.

TABLE 1

Foam Composition:		
Low Unsaturation Base Polyol	74	
Conventional Polyol		74
Polymer Polyol	26	26
Water	4.1	4.1

TABLE 1 (continued)

Foam Composition:		
DEOA	1.2	1.2
NiAx A-107	0.20	0.20
NiAx A-33	0.40	0.40
OSi Y-10,515	1.00	1.00
TDI	100 index	100 index
Polyol Properties		
Hydroxyl Number (mgKOH/g)	28	28
Polyol Functionality	2.3	2.2
Ethylene Oxide Content (wt.%)	15	15
Primary Hydroxyl Content (mol%)	22	75
Polyol Unsaturation (meq/g)	0.003	0.070
Foam Properties:		
	Low Unsat.	Conventional
Molded Part Density (lb/ft <sup>3</sup> )		1.80
Resiliency (%)		69
25% IFD (lbs)	Total Collapse	24
50% IFD (lbs)		44
65% IFD (lbs)		68
Tensile Strength (psi)		22
Elongation at Break (psi)		186
Tear Strength (lb/in)		1.55
75% Dry Compression Set (%)		7
50% Humid-Aged Compression Set (%)		18
50% Wet Compression Set (%)		32

[0047] Comparative Examples 1 and 2 illustrate that substitution of low monol, exclusively DMC-catalyzed polyol having low unsaturation for a conventional polyurethane molding polyol (high primary hydroxyl), despite having the same overall oxyethylene content, results in a foam system in which the foam totally collapses in one-shot molded foam.

#### **Example 1 and Comparative Example 3**

[0048] Molded foams were produced utilizing a prepolymer process with low unsaturation and conventional (high unsaturation, high monol content) polyether polyols of similar overall functionality. Two low monol, low unsaturation polyols, a triol and a diol, were blended to produce a base polyol composition which has an actual functionality similar to the control. Note that actual, or measured functionality is a measure of the actual polyol functionality and is not the "nominal" functionality, or functionality of the polyol starter, as is normally reported. These examples compare foams which are either entirely low monol or conventional (i.e., both base polyol and polymer polyol are either low unsaturation or conventional). The polymer solids content of each foam was identical, the difference in polymer polyol content the result of normalization of solids levels (the low unsaturation polymer polyol was 43 weight percent solids, the conventional polymer polyol, 38 weight percent solids).

[0049] The results shown below indicate significant and surprising improvements in firmness, tensile strength, elongation, tear strength, dry compression sets, humid-aged compression sets, wet sets, and the durability parameters: creep, load loss, and height loss, when prepolymers prepared from low unsaturation polyols are employed. Testing of dynamic properties is discussed in several articles, including "New Dynamic Flex Durability Test. 1", K. D. Cavender, 33RD ANNUAL POLYURETHANE TECHNICAL/MARKETING CONFERENCE, Sept. 30-Oct. 3, 1990, pp. 282-288; "Real Time Foam Performance Testing", K. D. Cavender, 34TH ANNUAL POLYURETHANE TECHNICAL/MARKETING CONFERENCE, Oct. 21-24, 1992, pp. 260-265; and "Real Time Test for Auto Seating Foam", SAE INTL. CONGRESS & EXPOSITION, Paper No. 930634, 1993.

TABLE 2

Prepolymer Composition	Low Unsaturation	Conventional
	Polyol	Polyol
Low Unsaturation Base Polyol <sup>1</sup> (OH=28)	73	-
Conventional Base Polyol <sup>2</sup> (OH=28)	-	70
Arcol 2580 <sup>4</sup>	4	4
Low Unsaturation Polymer Polyol <sup>3</sup>	23	-
Conventional Polymer Polyol <sup>5</sup>	-	26
TDI/MDI (80/20)	42	42
Polymer Solids Content	~10%	~10%
Base Polyol Functionality	~2.3	~2.2
Base Polyol Unsaturation (meq/g)	0.003	0.07
Foam Composition		
Low Unsaturation Prepolymer (above)	100	-
Conventional Prepolymer (above)	-	100
Water	2.5	2.5
OSi Nix A-1 Catalyst	0.25	0.25
Surfactant Blend (Tergitol 15-S- 9/DC5043)	1.1	1.1
Foam Properties		
Molded Part Density (lb/ft <sup>3</sup> )	2.3	2.3
Resiliency (%)	61	62
25% IFD (lbs)	38	33
50% IFD (lbs)	62	59
65% IFD (lbs)	84	83
Tensile Strength (psi)	20,2	14.7
Elongation at Break (psi)	178	135
Tear Strength (lb/in)	2.20	1.91
50% Dry Compression Set (%)	4.5	8.4
75% Dry Compression Set (%)	3,1	6.8
50% Humid-Aged Compression Set (%)	8.0	11.1
50% Wet Compression Set (%)	9.0	24.1
Dynamic Fatigue Properties		
Creep, %	8.0	9.2

<sup>1</sup> A polyoxypropylene/polyoxyethylene polyol containing 15 weight percent oxyethylene moieties prepared by the DMC-catalyzed oxyalkylation of a mixed diol/triol starter, having an unsaturation of c.a. 0.005 meq/g, a primary hydroxyl content of c.a. 30%, and a functionality of 2.3.

<sup>2</sup> A base (KOH) catalyzed polyoxypropylene/polyoxyethylene polyol having an unsaturation of 0.07 meq/g, a measured functionality of 2.2, and containing 15% by weight oxyethylene moieties as a cap.

<sup>3</sup> A polymer-modified polyol containing 43 weight percent of 37/63 acrylonitrile/styrene solids polymerized in situ in a 6000 Da m.w. polyoxypropylene/polyoxyethylene, DMC-catalyzed low unsaturation polyol containing 15% random oxyethylene moieties.

<sup>4</sup> A cell-opening polyol, conventionally catalyzed, having 75% oxyethylene and 25% oxypropylene moieties co-fed (random), and a hydroxyl number of 40.

<sup>5</sup> Polymer modified polyol similar to the low-unsaturation polymer modified polyol, but containing 38% solids, the base polyol unsaturation being c. a. 0.04 meq/g.

TABLE 2 (continued)

Dynamic Fatigue Properties		
Load Loss, %	15.6	21.8
Height Loss, %	1.4	2.4

[0050] Example 1 and Comparative Example 3 illustrate the unexpected and surprising increases in foam physical properties achieved when employing prepolymers based on low unsaturation polyols as compared to conventionally base-catalyzed polyol-derived prepolymers. Both foam formulations had the same solids content, contributed by the polymer-modified polyol used in prepolymer preparation. Noteworthy is the increase in 25% IFD, and the considerable improvements in both tensile strength (37% increase) and elongation at break (32% increase). The prior art suggests that improvement in one of the latter two properties would be expected to result in a decrease in the other of the two properties. The tear strength is increased also, but perhaps the most notable improvements are in both the dry and humid aged compression sets, and particularly the wet set performance, the latter showing a 67 percent improvement! Wet set is particularly important in molded seating, e.g. automotive seating, where exposure to hot, humid environments such as are found in the Southern United States and the tropics is expected.

[0051] In addition to the static properties discussed above, the subject foams also displayed noticeably improved dynamic fatigue properties, such as resistance to creep, load loss, and height loss, and demonstrated superior composite durability as well.

### Example 2

[0052] A molded foam was prepared from an isocyanate terminated prepolymer prepared by reacting 73 parts of a glycerine-initiated polyoxypropylene polyol having an unsaturation of 0.003 meq/g containing 15 weight percent random oxyethylene moieties and a primary hydroxyl content of 30 percent; 23 parts of a polymer polyol having 43% acrylonitrile/styrene (37/63) solids as the dispersed phase in a conventionally catalyzed base polyol having a hydroxyl number of 35 and 19% oxyethylene content; 4 parts ARCOL® 2580 polyether polyol, a conventionally catalyzed 40 hydroxyl number 75% oxyethylene/25% oxypropylene random polyol; with 42 parts of an 80/20 blend of TDI/MDI. The prepolymer was reacted with water, 3.5 parts; diethanolamine, 1.0 part; NIAx® A-1 amine catalyst 0.25 part; and Air Products DC5043 silicone surfactant, 1.0 part. Foam test results are presented below.

Foam Results:	
Molded Part Density (lb/ft <sup>3</sup> )	2.3
Resiliency (%)	66
25% IFD (lbs)	31
50% IFD (lbs)	53
65% IFD (lbs)	77
Tensile Strength (psi)	16.9
Elongation at Break (psi)	125
Tear Strength (lb/in)	1.52
50% Dry Compression Set (%)	5.8
75% Dry Compression Set (%)	5.3
50% Humid-Aged Compression Set (%)	8.5
50% Wet Compression Set (%)	11.0

### Example 4 and Comparative Example 6

[0053] In a manner similar to that disclosed in Example 1, further prepolymer formulations employing low unsaturation polyols and base-catalyzed polyols of similar functionality were employed to produce molded foam. The formulations and foam physical properties are given below in Table 4.

TABLE 4

	Low Unsaturation Polyol	Conventional Polyol
5	Prepolymer Composition	
	Low Unsaturation, 28 OH triol <sup>1</sup>	36.5
	Low Unsaturation, 28 OH diol <sup>2</sup>	36.5
	Conventional Polyol, 28 OH triol <sup>3</sup> Arcol 2580 (40 OH polyol)	73.4
10	Polymer Polyol <sup>4</sup>	23
	80/20 TDI/MDI Isocyanate Blend	42
	Base Polyol Functionality	~2.5
15	Foam Formulation	
	Low Unsaturation Polyol	100
	Conventional Polyol Prepolymer	100
	Water	2.5
20	OSi Nix A-1 Catalyst	0.18
	Surfactant Blend (UCC Tergitol 15-S-9/DC5043)	0.35
25	Foam Properties	
	Molded Density (lb/ft <sup>3</sup> )	2.3
	25% IFD (lbs.)	37
	65% IFD (lbs.)	82
30	Tensile Strength (psi)	18.0
	Elongation (%)	161
	Tear Strength (lb/in)	1.89
	50% Compression Set (%)	7.6
	75% Compression Set (%)	6.3
35	50% Humid Compression Set (%)	11.2
	50% Wet Set (%)	30.3

1 A polyoxypropylene/polyoxyethylene, oxypropylated glycerine oligomer initiated, random copolymer prepared by DMC catalysis containing 15% by weight oxyethylene moieties, a primary hydroxyl content of 30 mol percent, and an unsaturation of 0.005 meq/g.

2 A polyoxypropylene/polyoxyethylene, oxypropylated propylene glycol oligomer initiated random copolymer prepared by DMC catalysis containing 15% by weight oxyethylene moieties, a primary hydroxyl content of 30 mol percent, and an unsaturation of 0.005 meq/g.

3 A base-catalyzed (KOH) glycerine initiated polyoxypropylene/polyoxyethylene triol having an unsaturation of 0.07 meq/g, a functionality of 2.2, and containing 15 weight percent oxyethylene moieties as a cap.

4 Polymer-modified polyol containing 43% solids, the base polyol unsaturation being c.a. 0.04 meq/g.

[0054] As can be seen, consistent with prior examples, foam properties are considerably improved when molded foam is prepared from prepolymers derived from low unsaturation polyols are utilized.

#### Claims

1. A process for the preparation of molded polyurethane foam, comprising reacting, in a closed mold, a foam-forming reactive mixture comprising:

a) an isocyanate component comprising in major part an isocyanate-terminated prepolymer having an NCO group content of from about 5 to about 35 weight percent based on the weight of said isocyanate-terminated prepolymer, said isocyanate-terminated prepolymer prepared by the reaction of a stoichiometric excess of one or more di- or polyisocyanates with a polyol component containing a polyoxyalkylene polyether polyol portion prepared by double metal cyanide complex catalysis having an unsaturation of less than 0.03 meq

unsaturation per gram of polyoxyalkylene polyether polyol portion and a number average equivalent weight of about 1500 to about 5000; with

b) one or more isocyanate reactive component(s), at an isocyanate index of between 70 and 130; optionally in the presence of an effective amount of one or more catalysts which promote the reaction of a) with b), a cell-stabilizing effective amount of one or more surfactants; and an amount of blowing agent sufficient to provide a foam density between about 16 and 64 kg/m<sup>3</sup> (1.0 lb/ft<sup>3</sup> and 4.0 lb/ft<sup>3</sup>).

2. The process of claim 1 wherein said polyoxyalkylene polyether portion of said polyol component has a unsaturation of 0.02 meq unsaturation per gram of polyoxyalkylene polyether polyol portion.
3. A process as claimed in claim 1 **characterised in that** said polyoxyalkylene polyether polyol portion of said polyol component has a unsaturation of 0.01 meq unsaturation per gram of polyoxyalkylene polyether polyol portion.
4. A process as claimed in any one of the preceding claims **characterised in that** a majority of said polyol component comprises one or more higher polyoxyalkylene/polyoxyethylene polyether polyols having nominal functionalities between 2 and 8 and an average primary hydroxyl content of less than 70 mol percent based on the weights of said higher polyoxyalkylene/polyoxyethylene polyether polyols.
5. A process as claimed in claim 4 **characterised in that** the said average primary hydroxyl content is less than 50 mol percent based on the weights of said polyoxypropylene/polyoxyethylene polyether polyols.
6. A process as claimed in any one of the preceding claims **characterised in that** a majority of said polyol component comprises one or more polyoxypropylene/polyoxyethylene polyether polyols, each having an unsaturation less than about 0.015 meq/g, each having at least one terminal block comprising random oxyethylene and oxypropylene moieties, and each having a primary hydroxyl content of less than about 50 mol percent.
7. A process as claimed in any one of the preceding claims **characterised in that** a minor amount of said polyol component comprises a polyoxypropylene/polyoxyethylene polyether polyol having a polyoxyethylene cap such that said polyoxypropylene/polyoxyethylene polyether polyol has a primary hydroxyl content greater than 50 mol percent.
8. A process as claimed in any one of the preceding claims **characterised in that** said polyol component comprises a polymer-modified polyol.
9. A process as claimed in any one of claims 1 to 8 **characterised in that** a majority of said polyol component comprises one or more higher polyoxyalkylene/polyoxyethylene polyether polyols and/or polymer-modified higher polyoxyalkylene/polyoxyethylene polyether polyols each having an unsaturation of less than about 0.01 meq/g, a nominal functionality of from 2 to 8, a number of average equivalent weight between about 800 Da to 5000 Da, and a primary hydroxyl content of less than about 50 mol percent.
10. A process as claimed in claim 9 **characterised in that** the number average equivalent weight of at least one of said one or more higher polyoxyalkylene/polyoxyethylene polyether polyols and/or polymer-modified higher polyoxyalkylene/polyoxyethylene polyether polyols is between about 1500 Da and 3000 Da.
11. A process as claimed in any one of the preceding claims **characterised in that** said isocyanate reactive component includes one or more polyoxyalkylene polyols.
12. A process as claimed in claim 11 **characterised in that** said one or more polyoxyalkylene polyols together have an average unsaturation of less than 0.03 meq/g.
13. A process as claimed in claim 11 or claim 12 **characterised in that** at least a portion of said one or more polyoxyalkylene polyols has a primary hydroxyl content of greater than about 70 mol percent.
14. A process as claimed in claim 13 **characterised in that** said polyoxyalkylene polyol having a primary hydroxyl content of 70 mol percent or more comprises a polyoxypropylene/polyoxyethylene polyether polyol containing at least one polyoxyethylene terminal block.
15. A process as claimed in any one of the preceding claims **characterised in that** said isocyanate reactive component

includes water which further serves as a reactive blowing agent.

16. A process as claimed in claim 15 **characterised in that** water is the sole blowing agent.

17. A process as claimed in any one of the preceding claims **characterised in that** said isocyanate reactive component includes a chain extender and/or cross-linker.

18. A process as claimed in claim 17 **characterised in that** said chain extender or cross-linker comprises less than about 5 per cent based on the weight of the foam.

19. A process as claimed in claim 17 or claim 18 **characterised in that** said cross-linker is selected from alkanol amines.

20. A process as claimed in claim 19 **characterised in that** said cross-linker is selected from diethanolamine and triethanolamine.

21. A process as claimed in claim 1 **characterised in that** said di- or polyisocyanate is selected from the group consisting of TDI, MDI, or mixtures thereof; said polyol component has an average unsaturation of less than 0.02 meq/g and comprises in substantial part one or more polyoxypropylene/polyoxyethylene polyether polyols and/or polymer-modified polyoxypropylene/polyoxyethylene polyether polyols, each having an unsaturation less than about 0.01 meq/g and a primary hydroxyl content of less than about 50 mol percent; wherein said isocyanate reactive component comprises water as a sole blowing agent and further contains less than about 5 weight percent based on the weight of the foam of an alkanolamine cross-linker.

22. A polyurethane molded foam **characterised in that** it is prepared by a process as claimed in any one of claims 1 to 21.

23. A foam as claimed in claim 22 **characterised in that** the wet set is less than about 15%.

24. A foam as claimed in claim 22 **characterised in that** the wet set is less than about 10%.

#### Patentansprüche

1. Verfahren zur Herstellung eines geformten Polyurethanschaums, das die Umsetzung einer schaumbildenden, reaktiven Mischung, umfassend

a) eine Isocyanat-Komponente, die als Hauptteil ein isocyanat-terminiertes Prepolymer mit einem NCO-Gruppengehalt von etwa 5 bis etwa 35 Gew.-%, bezogen auf das Gewicht des isocyanat-terminierten Prepolymers, umfasst, wobei das isocyanat-terminierte Prepolymer durch Umsetzung eines stöchiometrischen Überschusses eines oder mehrerer Di- oder Polyisocyanate mit einer Polyol-Komponente hergestellt wird, die einen Polyoxyalkylenpolyetherpolyol-Anteil - der durch die Doppelmetallcyanidkomplex-Katalyse hergestellt wird - enthält, der eine Nichtsättigung von weniger als 0,03 Milliäquivalenten Nichtsättigung pro g Polyoxyalkylenpolyetherpolyol-Anteil und ein Zahlenmittel des Äquivalentgewichts von etwa 1500 bis etwa 5000 aufweist; mit b) einer isocyanatreaktiven Komponente oder mehreren isocyanatreaktiven Komponenten mit einem Isocyanatindex zwischen 70 und 130; gegebenenfalls in Gegenwart einer wirksamen Menge eines oder mehrerer Katalysatoren, welche die Umsetzung von a) mit b) fördern, einer wirksamen Zellenstabilisierenden Menge eines oder mehrerer Tenside, und einer Menge eines Treibmittels, die ausreichend ist, um eine Schaumdichte zwischen etwa 16 und 64 kg/m<sup>3</sup> (1,0 lb/ft<sup>3</sup> und 4,0 lb/ft<sup>3</sup>) bereitzustellen,

in einem geschlossenen Werkzeug umfasst. -

2. Verfahren gemäß Anspruch 1, worin der Polyoxyalkylenpolyetherpolyol-Anteil der Polyol-Komponente eine Nichtsättigung von 0,02 Milliäquivalenten Nichtsättigung pro g Polyoxyalkylenpolyetherpolyol-Anteil aufweist.

3. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Polyoxyalkylenpolyetherpolyol-Anteil der Polyol-Komponente eine Nichtsättigung von 0,01 Milliäquivalenten Nichtsättigung pro g Polyoxyalkylenpolyetherpolyol-Anteil aufweist.

4. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** ein Hauptteil der Polyol-Komponente ein oder mehrere höhere Polyoxyalkylen/Polyoxyethylen-Polyetherpolyole mit nominellen Funktionalitäten zwischen 2 und 8 und einem durchschnittlichen Gehalt an primärem Hydroxyl von weniger als 70 Mol-%, bezogen auf die Gewichte der höheren Polyoxyalkylen/Polyoxyethylen-Polyetherpolyole, umfasst.
5. Verfahren gemäß Anspruch 4, **dadurch gekennzeichnet, dass** der durchschnittliche Gehalt an primärem Hydroxyl geringer als 50 Mol-%, bezogen auf Gewichte der höheren Polyoxypropylen/Polyoxyethylen-Polyetherpolyole, ist.
6. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** ein Hauptteil der Polyol-Komponente ein oder mehrere Polyoxypropylen/Polyoxyethylen-Polyetherpolyole umfasst, die jeweils eine Nichtsättigung von weniger als etwa 0,015 Milliäquivalenten/g aufweisen, jeweils wenigstens einen terminalen Block aufweisen, der statistische Oxyethylen- und Oxypropylen-Reste umfasst, und jeweils einen Gehalt an primärem Hydroxyl von weniger als etwa 50 Mol-% aufweisen.
7. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** ein kleinerer Teil der Polyol-Komponente ein Polyoxypropylen/Polyoxyethylen-Polyetherpolyol mit einer Polyoxyethylen-Verkapselung umfasst, so dass das Polyoxypropylen-Polyoxyethylen-Polyetherpolyol einen Gehalt an primärem Hydroxyl von mehr als 50 Mol-% aufweist.
8. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Polyol-Komponente ein Polymer-modifiziertes Polyol umfasst.
9. Verfahren gemäß irgendeinem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** ein Hauptteil der Polyol-Komponente ein oder mehrere höhere Polyoxyalkylen/Polyoxyethylen-Polyetherpolyole und/oder Polymer-modifizierte höhere Polyoxyalkylen/Polyoxyethylen-Polyetherpolyole umfasst, die jeweils eine Nichtsättigung von weniger als etwa 0,01 Milliäquivalenten/g, eine nominelle Funktionalität von 2 bis 8, ein Zahlenmittel des Äquivalentgewichts zwischen etwa 800 Da und 5000 Da und einen Gehalt an primärem Hydroxyl von weniger als etwa 50 Mol-% aufweisen.
10. Verfahren gemäß Anspruch 9, **dadurch gekennzeichnet, dass** das Zahlenmittel des Äquivalentgewichts wenigstens eines oder mehrerer der höheren Polyoxyalkylen/Polyoxyethylen-Polyetherpolyole und/oder der Polymer-modifizierten höheren Polyoxyalkylen/Polyoxyethylen-Polyetherpolyole zwischen etwa 1500 Da und 3000 Da liegt.
11. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die isocyanatreaktive Komponente ein oder mehrere Polyoxyalkylenpolyole einschließt.
12. Verfahren gemäß Anspruch 11, **dadurch gekennzeichnet, dass** ein oder mehrere Polyoxyalkylenpolyole zusammen eine durchschnittliche Nichtsättigung von weniger als 0,03 Milliäquivalenten aufweisen.
13. Verfahren gemäß Anspruch 11 oder Anspruch 12, **dadurch gekennzeichnet, dass** wenigstens ein Anteil des einen oder der mehreren Polyoxyalkylenpolyole einen Gehalt an primärem Hydroxyl von mehr als etwa 70 Mol-% aufweist.
14. Verfahren gemäß Anspruch 13, **dadurch gekennzeichnet, dass** das Polyoxyalkylenpolyol, das einen Gehalt an primärem Hydroxyl von 70 Mol-% oder mehr aufweist, Polyoxypropylen/polyoxyethylen-Polyetherpolyol umfasst, das wenigstens einen Polyoxyethylen-terminalen Block enthält.
15. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die isocyanatreaktive Komponente Wasser einschließt, das weiterhin als reaktives Treibmittel dient.
16. Verfahren gemäß Anspruch 15, **dadurch gekennzeichnet, dass** Wasser das einzige Treibmittel ist.
17. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die isocyanatreaktive Komponente einen Kettenverlängerer und/oder ein Vernetzungsmittel enthält.
18. Verfahren gemäß Anspruch 17, **dadurch gekennzeichnet, dass** der Kettenverlängerer oder das Vernetzungsmittel weniger als etwa 5 %, bezogen auf das Gewicht des Schaums, ausmacht.



19. Verfahren gemäß Anspruch 17 oder Anspruch 18, **dadurch gekennzeichnet**, dass das Vernetzungsmittel aus Alkanolaminen ausgewählt ist.
20. Verfahren gemäß Anspruch 19, **dadurch gekennzeichnet**, dass das Vernetzungsmittel aus Diethanolamin und Triethanolamin ausgewählt ist.
21. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet**, dass das Di- oder Polyisocyanat aus der aus TDI, MDI oder Mischungen derselben bestehenden Gruppe ausgewählt ist; die Polyol-Komponente eine durchschnittliche Nichtsättigung von weniger als 0,02 Milliäquivalenten/g hat und als Hauptteil ein oder mehrere Polyoxypropylen/Polyoxyäthylen-Polyetherpolyole und/oder Polymer-modifizierte Polyoxypropylen/Polyoxyäthylen-Polyetherpolyole umfasst, die jedes eine Nichtsättigung von weniger als etwa 0,01 Milliäquivalenten/g und einen Gehalt an primärem Hydroxyl von weniger als etwa 50 Mol-% aufweisen; worin die isocyanatreaktive Komponente Wasser als einziges Treibmittel umfasst und weiterhin weniger als etwa 5 Gew.-%, bezogen auf das Gewicht des Schaums, eines Alkanolamin-Vernetzungsmittels enthält.
22. Geformter Polyurethanschaum, **dadurch gekennzeichnet**, dass er durch ein Verfahren gemäß irgendeinem der Ansprüche 1 bis 21 hergestellt wird.
23. Schaum gemäß Anspruch 22, **dadurch gekennzeichnet**, dass die Nasshärtung geringer als etwa 15 % ist.
24. Schaum gemäß Anspruch 22, **dadurch gekennzeichnet**, dass die Nasshärtung geringer als 10 % ist.

#### Revendications

1. Procédé de préparation d'une mousse de polyuréthane moulée, comprenant la réaction, dans un moule fermé, d'un mélange réactif formant une mousse comprenant
  - a) un constituant isocyanate comprenant en majeure partie un prépolymère à terminaison isocyanate, ayant une teneur en groupes NCO d'environ 5 à environ 35 % en masse par rapport à la masse dudit prépolymère à terminaison isocyanate, ledit prépolymère à terminaison isocyanate étant préparé par réaction d'un excès stoechiométrique d'un ou plusieurs di- ou polyisocyanates avec un constituant polyol contenant une portion polyoxyalkylène-polyétherpolyol préparé par catalyse avec un complexe de cyanure de métal double, ayant une insaturation inférieure à 0,03 méq d'insaturation par gramme de portion polyoxyalkylène-polyétherpolyol et une masse équivalente moyenne en nombre d'environ 1 500 à environ 5 000; avec
  - b) un ou plusieurs constituants réagissant avec les isocyanates, à un indice d'isocyanate compris entre 70 et 130; éventuellement en présence d'une quantité efficace d'un ou plusieurs catalyseurs qui favorisent la réaction de a) avec b), d'une quantité efficace pour la stabilisation des cellules d'un ou plusieurs agents tensioactifs; et d'une quantité d'agent gonflant suffisante pour donner une densité de mousse comprise entre environ 16 et 64 kg/m<sup>3</sup> (entre environ 1,0 et 4,0 lb/ft<sup>3</sup>).
2. Procédé selon la revendication 1, dans lequel ladite portion polyoxyalkylène-polyéther dudit constituant polyol a une insaturation de 0,02 méq d'insaturation par gramme de portion polyoxyalkylène-polyétherpolyol.
3. Procédé selon la revendication 1, **caractérisé en ce que** ladite portion polyoxyalkylène-polyétherpolyol dudit constituant polyol a une insaturation de 0,01 méq d'insaturation par gramme de portion polyoxyalkylène-polyétherpolyol.
4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la majeure partie dudit constituant polyol comprend un ou plusieurs polyoxy(alkylène supérieur)/polyoxyéthylène-polyétherpolyols ayant des fonctionnalités nominales comprises entre 2 et 8 et une teneur en groupes hydroxyle primaires inférieure à 70 % en mol par rapport aux masses desdits polyoxy(alkylène supérieur)/polyoxyéthylène-polyétherpolyols.
5. Procédé selon la revendication 4, **caractérisé en ce que** ladite teneur en groupes hydroxyle primaires est inférieure à 50 % en mol par rapport aux masses desdits polyoxy(alkylène supérieur)/polyoxyéthylène-polyétherpolyols.
6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la majeure partie dudit constituant polyol comprend un ou plusieurs polyoxypropylène/polyoxyéthylène-polyétherpolyols ayant chacun une insaturation inférieure à environ 0,015 méq/g, ayant chacun au moins un bloc terminal comprenant des fragments

oxyéthylène et oxypropylène statistiques, et ayant chacun une teneur en groupes hydroxyle primaires inférieure à environ 50 % en mol.

- 5 7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'une** quantité mineure dudit constituant polyol comprend un polyoxypropylène/polyoxyéthylènepolyétherpolyol ayant une coiffe polyoxyéthylène telle que ledit polyoxypropylène/polyoxyéthylènepolyétherpolyol a une teneur en groupes hydroxyle primaires supérieure à 50 % en mol.
- 10 8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit constituant polyol comprend un polyol modifié par un polymère.
- 15 9. Procédé selon l'une quelconque des revendications 1 à 8, **caractérisé en ce que** la majeure partie dudit constituant polyol comprend un ou plusieurs polyoxy(alkylène supérieur)/polyoxyéthylènepolyétherpolyols et/ou polyoxy(alkylène supérieur)/polyoxyéthylènepolyétherpolyols modifiés par un polymère ayant chacun une insaturation inférieure à environ 0,01 méq/g, une fonctionnalité nominale comprise entre 2 et 8, une masse équivalente moyenne en nombre comprise entre environ 800 Da et 5 000 Da, et une teneur en groupes hydroxyle primaires inférieure à environ 50 % en mol.
- 20 10. Procédé selon la revendication 9, **caractérisé en ce que** la masse équivalente moyenne en nombre d'au moins l'un desdits un ou plusieurs polyoxy(alkylène supérieur)/polyoxyéthylènepolyétherpolyols et/ou polyoxy(alkylène supérieur)/polyoxyéthylènepolyétherpolyols modifiés par un polymère est comprise entre environ 1 500 Da et 3 000 Da.
- 25 11. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit constituant réagissant avec les isocyanates comprend un ou plusieurs polyoxyalkylènepolyols.
- 30 12. Procédé selon la revendication 11, **caractérisé en ce que** lesdits un ou plusieurs polyoxyalkylènepolyols ont ensemble une insaturation moyenne inférieure à 0,03 méq/g.
- 35 13. Procédé selon la revendication 11 ou la revendication 12, **caractérisé en ce qu'au moins** une portion desdits un ou plusieurs polyoxyalkylènepolyols a une teneur en groupes hydroxyle primaires supérieure à environ 70 % en mol.
- 40 14. Procédé selon la revendication 13, **caractérisé en ce que** ledit polyoxyalkylènepolyol ayant une teneur en groupes hydroxyle primaires supérieure à 70 % en mol comprend un polyoxypropylène/polyoxyéthylènepolyétherpolyol contenant au moins un bloc terminal polyoxyéthylène.
- 45 15. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit constituant réagissant avec les isocyanates comprend de l'eau, qui sert en outre d'agent gonflant réactif.
- 50 16. Procédé selon la revendication 15, **caractérisé en ce que** l'eau est le seul agent gonflant.
- 55 17. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** ledit constituant réagissant avec les isocyanates comprend un agent d'allongement de chaîne et/ou un agent réticulant.
18. Procédé selon la revendication 17, **caractérisé en ce que** ledit agent d'allongement de chaîne ou réticulant constitue moins d'environ 5 % de la masse de la mousse.
19. Procédé selon la revendication 17 ou la revendication 18, **caractérisé en ce que** ledit agent réticulant est choisi parmi des alcanolamines.
20. Procédé selon la revendication 19, **caractérisé en ce que** ledit agent réticulant est choisi parmi la diéthanolamine et la triéthanolamine.
21. Procédé selon la revendication 1, **caractérisé en ce que** ledit di- ou polyisocyanaté est choisi dans le groupe constitué par le TDI, le MDI ou leurs mélanges; ledit constituant polyol a une insaturation moyenne inférieure à 0,02 méq/g et comprend une fraction importante d'un ou plusieurs polyoxypropylène/ polyoxyéthylènepolyétherpolyols et/ou polyoxypropylène/polyoxyéthylènepolyétherpolyols modifiés par un polymère, ayant chacun une

saturation inférieure à environ 0,01 méq/g et une teneur en groupes hydroxyle primaires inférieure à environ 50 % en mol; ledit constituant réagissant avec les isocyanates comprend de l'eau comme seul agent gonflant et contient en outre moins d'environ 5 % en masse, par rapport à la masse de la mousse, d'un agent réticulant de type alcanolamine.

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**22.** Mousse de polyuréthane moulée, caractérisée en ce qu'elle est préparée par un procédé selon l'une quelconque des revendications 1 à 21.

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**23.** Mousse selon la revendication 22, caractérisée en ce que la déformation à l'état humide est inférieure à environ 15 %.

**24.** Mousse selon la revendication 22, caractérisée en ce que la déformation à l'état humide est inférieure à environ 10 %.

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